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Effects of titania based catalysts on in-situ pyrolysis of *Pavlova* microalgae

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ABSTRACT

Pavlova microalga was pyrolysed in presence of titania based catalysts in a fixed bed reactor at various temperatures. The effects of catalysts on *Pavlova* microalga pyrolysis was investigated. A large fraction of the starting energy (~63-74 % daf) was recovered in the bio-oils when the catalysts were used. The bio-oil yield was 20% higher in presence of Ni/TiO_2 (22.55 wt.%) at 500 °C. The High Heating Values of the produced bio-oils were in the range of ~35-37 MJ/kg and suffered strong deoxygenation, with O content (% daf) diminished from 51 wt.% to ~9-12 wt.%. The ^1H Nuclear Magnetic Resounance and Gas Chromatography Mass Spectrometry suggested that the titania catalysts enlarged the aliphatics and aromatic compounds and decreased oxygenates in the bio-oils. Ni/TiO_2 had the greatest activity in increasing aliphatic protons (60%) and decreasing coke formation. Its enhanced cracking activity was due to its higher availability on the catalyst surface, compared to Co and Ce, and to strong interaction between Ni and TiO_2 support. Despite the fact that the bio-oils were partially de-nitrogenated, the N-content still represent a major limitation for their use as bio-fuels without further upgrading.

***Keywords*:** Bio-oil, *Pavlova*, Pyrolysis, deoxygenation, Catalyst, Titania

1. Introduction

Microalgae are promising feedstock for bio-fuels, chemicals, food, cosmetics and healthcare and have been cultivated in open pounds or raceways as human and animal feed supplements on an industrial scale [1-3]. Microalgae have several advantages over terrestrial crops: (i) can grow in open water such as sea water and ponds or in photobioreactors on non-arable lands ii) have higher lipid content (some up to 80 %) iii) do not compete with food crops (iv) have higher CO_2 capture capacity and can remove and recycle nutrients from waste water and flue gases [4-5]. Over the decades, different approaches for the production of bio-fuels from microalgae have emerged, such as biogas from anaerobic digestion, biodiesel (from fatty acids), hydrogen (from gasification) and bio-oils from liquefaction and pyrolysis [6,7]. Microalgae contain three main components in varying amounts: lipids (3–50 wt%), carbohydrates (10–50 wt%) and proteins (6– 65 wt%).

Compared to more established routes such as algal fatty acids to biodiesel, the thermochemical conversion of algae can advantagiously convert completely the algal biomass, which makes the process more attractive [5]. In recent years, pyrolysis of both lignocellulosic and algal biomass has been widely investigated. Pyrolysis refers to thermal depolymerisation or organics at moderate temperatures (400–600 °C) in absence of oxygen.

One of the most challenging barriers to the thermo-chemical conversion pathway is the high moisture content of microalgae. A study indicates that mechanical dewatering prior a 2000 t/day microalgae catalytic pyrolysis facility, can produce 21.4 million gallons of biofuel per year at a cost of $1.49 per liter, which is similar to the gasoline cost range in Europe in 2016 (~1.2-1.7 $ per liter, globalpetrolprices) [8] .

Pyrolysis of many algal species has been studied including Nannochloropsis, Chlorella, Tetraselmis, Isochrysis and Microcystis. In a previous study, Miao et al. [9] performed the fast pyrolysis of Chlorella prothothecoides and Microcystis aeruginosa species grown

phototrophically. They obtained bio-oil yields of 18% and 24% with HHVs of 30MJ/kg and 29MJ/kg, respectively. Belotti et al. [10] studied the pyrolysis of Chlorella vulgaris grown in complete and nitrogen starved medium. They found that the fast pyrolysis of nitrogen starved Chlorella vulgaris yielded 42.2% of bio-oil at 400 °C. The bio-oil produced from nitrogen starved algae had higher amount of fatty acids and lower amount of nitrogenous species, resulting in an improved quality.

Although pyrolysis is recently attracting rising interest for the producing of liquid fuels, the resulting bio-oils have several drawbacks, such as low heating value, high viscosity, high oxygen content and high acidity, whichlimit their widespread use and need to be upgraded first. Catalytic fast pyrolysis involves the catalytic conversion of primary pyrolysis vapours to less oxygenated liquid fuels by eliminating oxygen as CO, H_2O and CO_2 [11]. The catalysts can be added directly to biomass in the pyrolysis reactor or added in a downstream reactor to upgrade the hot pyrolysis vapours [12]. Acidic metal oxides (e.g.Al_2O_3), sulfated metal oxides (e.g. SO_4^{2-}/TiO_2) and transition metal oxides (e.g. CeO_2, TiO_2) have been investigated as catalysts in lignocellulosic materials pyrolysis [13-16]. Metal oxides such as TiO_2 and CeO_2 catalysts decreased the liquid and organic product yields and increased gas, water, and solid products yields; where carboxylic acids like acetic acid were transformed to gasoline-range organics, by elimination of O_2 as CO_2 and water [15,17]. CeO_2 was found to be highly performing for this scope and also tolerant to water. Employing Al_2O_3 and TiO_2 as supports or doping them with a strong base improved their catalytic activity [12]. Other intensily investigated catalysts for microalgae pyrolysis are Na_2CO_3 and ZSM-5-based zeolites [18-21]. Na_2CO_3 tend to increase the gas yields while decreasing the bio-oil yield, in which an energy recovery of 40% of bio-oil was achieved [19]. HZSM-5 increased the hydrocarbons fraction and in particular the aromatics [20]. For example, Chlorella sp. bio-oils (43-50 wt%) was enriched in hydrocarbons in the organic phase (from 21 wt% in absence of catalyst to 43 wt%) [21].

Pavlova sp. is known to be able to synthesize DHA and EPA (essential n-3 PUFA) in larger amounts. The potential of the *Pavlova* sp. as n-3 PUFA source in marine fish nutrition was investigated by Rehberg-Haas [22]. However, there is no reported study regarding the evaluation of *Pavlova sp.* as a biomass feedstock for bio-oil generation. Since characteristics such as low cost, availability, sustainability, resistance to attrition and catalytic activity are important criteria for the selection of catalysts, there is a great interest in developing catalysts from non-nobel metals and rare materials. Under this scenario, TiO_2 represents a promising candidate as catalyst for biomass conversion technologies. Kaewpengkrow et al. [23] performed the catalytic upgrading of pyrolysis vapors from Jatropha wastes using alumina, zirconia and titania. They found that alumina and titania yielded high hydrocarbons and less oxygenates, while hydrocarbon selectivity was the highest with titania based catalysts. Lu et al. [24] studied the catalytic fast pyrolysis of cellulose mixed with sulphated titania to produce levoglucosenone. They found that the SO_4^{2-}/TiO_2 (anatase) decreased the early cellulose breakdown temperature and changed the pyrolytic product considerably resulting the best catalyst for levoglucosenone production. Mante et al. [25] used anatase TiO_2 nanorods, CeOx–TiO_2 mixed oxides, pure CeO_2, ZrO_2, and MgO as catalysts for the catalytic conversion of biomass pyrolysis vapors into hydrocarbons. Ceria-based catalysts resulted very effective in producing ketones.

The cracking properties of nickel, ceria and titania can be advantageous to the in-situ removal of oxygen from the microalgal bio-oils. To the best of our knowledge, there is no single study available in the literature on the comparison of product yields and compositions of bio-oils attained by catalytic pyrolysis of *Pavlova* microalga with titania based catalysts and their deoxygenation effect. Accordingly, the aim of this study is to screen and compare the effects of ceria and titania based catalysts on *Pavlova* pyrolysis yield and products selectivity.

2. Experimental

2.1 Feedstock preparation

Pavlova sp. was acquired fromVaricon Aqua Solutions. The biochemical composition of *Pavlova* algae in terms of proteins, carbohydrates and lipids was also provided by Varicon Aqua Solutions. The microalgae were dried in an oven at 50 °C, milled to a particle size between 80 and 140 meshes (105-174 μm) and stored in a desiccator for further use.

2.2. Catalyst preparation and characterization

Commercial ceria (CeO_2) and titania (TiO_2) nanopowders were purchased from Sigma-Aldrich. Titania (TiO_2) based catalysts were prepared according to the procedure shown in Fig. S1. As shown in Fig. S1, metal based TiO_2 sols were prepared firstly by refluxing a solution containing titanium (IV) butoxide, propan-2-ol, nitric acid and fixed amount of cerium (III) nitrate ($Ce(NO_3)_3.6H_2O$), cobalt (II) acetylacetonate ($Co(C_5H_7O_2)_2$) or nickel (II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) using an oil bath at around 95°C for 24 hours. After the reflux period, the resulting sol was dried and calcined in a furnace (Carbolite, CWF 1100) under airflow at the rate of 1°C min^{-1} to 100 °C for 12 h.

The physical characteristics of the different catalysts were determined by N_2 adsorption method at -195.8 °C using Micromeritics Gemini VII instrument [5], while Quantachrome Instruments Autosorb IQ Station 2 was used for the titania based catalysts. The catalysts were outgassed overnight at 180 °C. Brunauer–Emmett–Teller (BET) and the Barrett–Joyner–Halenda (BJH) equations were used for determining the materials surface and pore size distribution/volume. The mineral phases and elemental composition of the catalysts were checked by powder X-ray diffraction using a Bruker D8 Advance powder diffractometer (Ge-monochromated Cu *K*α1 radiation; wavelength=1.5406 Å, 40 kV, 30 mA) with Sol-X Energy Dispersive detector. The data were obtained over the angular range 5°-85° degrees in two-theta under atmospheric pressure.

2.3. Feedstock and products analyses

2.3.1. Proximate and ultimate analysis

The proximate analyses were conducted according to ASTM standarts (D2016, E872-82, D1102-84). C, N and H were determined using LECO CHNS-932 analyzer, while O content was obtained by difference. Higher heating values (HHV) of samples were obtained using the Dulong's Formula [23].

2.3.2. Proton nuclear magnetic resonance (^{1}H NMR) analysis

^{1}H NMR analyses were performed using a Bruker Avance III operatingat 400 MHz. The samples were dissolved in $CDCl_3$ (1:1 volume ratio) and TMS (tetramethylsilane) was used a internal standard.

2.3.3. TGA analysis

Thermogravimetric analysis (TGA) was carried out using a TA Q500 in presence of N_2 for determining volatiles and in presence of air to determine the fixed carbon and ash content. The method used is described in details in a previous work [13].

2.3.4. Gas chromatography–Mass spectrometry (GC–MS) analysis

An Agilent GC-MS 7890A/5975C series (column: HP 235–INNOWAX; transfer line at 270 °C, ion source at 250 °C and electron energy of 70 eV) was used for the GC-MS analysis of the bio-oils [26]. The bio-oil components were identified using mass spectral libraries (PMW_Tox3.l, Wiley7n.1 and NIST05a.L).

2.3.5. Coke analysis

Coke yield on catalysts was determined by the weight change during combustion using an Exstar TG/DTA 7200 in a 70 mL/min air flow. In a typical run, approximately10 mg of

sample was placed in the ceramic crucible and heated from 25 °C to the final temperature of 900 °C at a rate of 10 °C/min.

2.4. Pyrolysis experiments

The pyrolysis experiments of *Pavlova* were performed using a semi-fixed-bed reactor. The set-up was previously descibed [26]. The catalytic and non-catalytic algae pyrolysis experiments were performed at temperatures of 450, 500 and 550 ^{o}C at a constant heating rate 100 ^{o}C/min under N_2 atmosphere with a flow rate of 545 ml/min. The reactor temperature was kept constant at the final temperature for 60 min.

Actual pyrolysis tests were performed feeding 3 g of material per test (1.5g Pavlova and 1.5g catalyst). The bio-oils were recovered in three Dreshel bottles immersed in a ice-water bath with temperature kept constant at 0°C.

The remaining solid was recorded as bio-char yield (subtracting the catalyst weight). The amount of gaseous products was calculated by subtraction of solid and bio-oil yields from the amount of initial raw material.

The distribution of the parent algal material energy in the pyrolysis products was based on the pyrolysis material balance and HHV of bio-oils and bio-chars. The energy content of each product (bio-char and bio-oil) was calculated by multiplying the HHVs to the wt% of the products recovered. The energy content of bio-gas was calculated by subtracting the energy content of the bio-char and bio-oil from the starting energy content of the raw material (microalgae) [13].

3. Results and discussion

3.1. Feedstock characterization

Ultimate and proximate analyses of *Pavlova* were performed and the results are reported in Table S1. This alga strain has large protein content (43%) and a moderate amount of lipids

(20%) and carbohydrates (26%). The *Pavlova* moderate lipid content reduces this microalga suitability for biodiesel production, but enhances its suitability for pyrolysis. The large protein content, which was similar to that of other algal species such as *Scenedesmus obliquus*, *Chlorella vulgaris* and *Spirulina platensis* [27], resulted in high nitrogen content (4.81%). Ash content (24.45%) and fixed carbon (11.60%) were rather great compared to values of other algae species [28]. The decomposition behaviour of *Pavlova* was estimated using TGA/DTG (Fig. S2). According to Fig.S2, the *Pavlova* decomposition occurs between 105 and 800 °C (53. 9 % weight loss) that includes three main steps (at 130, 250, 455°C), corresponding to carbohydrates, proteins and lipids volatilisation [5]. The material left behind (40 %) at 800 °C, represents the fixed carbon and ash.

3.2. Catalyst characterization

Table 1 shows the surface area, pores size and volume of the synthetised catalysts assessed using N_2 adsorption isotherms at 77 K. The addition of metal oxides to TiO_2 influenced its catalyst properties. When we look at the loaded TiO_2 based catalysts, we see that there were clear differences between them. The specific surface areas (SBET) of Ce/TiO_2, Co/TiO_2 and Ni/TiO_2 catalysts were 126.80, 278.50 and 229.60 m^2/g, respectively, while starting TiO_2 had only ~9.5 m^2/g. All synthetised catalysts had a pore distribution between 17 and 300 Å, indicating the presence of micropores (<20 Å) and mesopores (>20 Å). Ni/TiO_2 had an average pore size of 58.06 Å (similar to the starting TiO_2), while Co/TiO_2 and Ce/TiO_2 had smaller average pore size (~29-31 Å). This may indicate that Co and Ce are deposited in the pores partially reducing their size.

The X-ray diffraction patterns of the prepared catalysts with TiO_2 support are shown in the Supplementary data (Fig. S3), which shows the X-ray diffraction patterns of metal loaded nanoparticles of Ni/TiO_2, Co/TiO_2 and Ce/TiO_2. Tetragonal anatase phase was confirmed by Powder Diffraction Standards (JCPDS) Card File no. 21-1272. Additional peaks of brookite at

198 ca. 31.4° were further observed in the metal loaded nanoparticles. Only small diffraction peaks
199 of metal oxides (NiO, CoO and CeO_2) phase were detected for the samples as they are hidden
200 from the large peaks of TiO_2. This could be due to their occurrence being in highly dispersed
201 phase within TiO_2 matrix or due to detectable limit of the diffractometer. EDS analysis
202 confirmed the elemental composition as 1.6wt%, 3.98wt% and 1.36wt% for Co, Ce and Ni
203 loaded TiO_2 catalysts, respectively.

204 3.3. Effect of temperature on products distribution

205 The total volatiles (bio-oil+gas yields) and distribution of products obtained by
206 pyrolysis of Pavlova with titania based catalysts with (1:1 ratio) and without catalyst is given
207 in Table 2. High char yields were probably due to the slow heating rate used (100°C/min) during
208 pyrolysis [29]. For example, when temperature was increased from 450 to 550 ^oC, the
209 conversion (total volatiles) was increased from 51% to 61% in the non-catalytic runs and from
210 52% to 63.7% in the catalytic runs with CeO_2. Similar trend was observed with TiO_2 catalysts.
211 The higher bio-oil yield was obtained at 500 ^oC, with Ni/TiO_2 producing the highest (22.5
212 wt%). The bio-oil yields were increased first at 500^oC and then decreased at 550 ^oC. This result
213 is in accordance with previous work [30].

214 3.4. Effect of catalysts on product distribution

215 Catalytic pyrolysis favours deoxygenation by removal of CO, CO_2 and H_2O [26,31].
216 When we look at the effect of titania based catalysts used in this study, we see that all had a
217 positive effect and increased the total volatiles compared to non-catalytic runs, with Ni/TiO_2
218 being the most effective.

219 The use of a neutral catalyst support (TiO_2) that does not promote acid catalyzed
220 polymerization of the various components of *Pavlova* increase the conversion of char, when
221 coupled with cracking metals such as Ni. Iliopoulou et al. found out that the addition of NiO to

222 a zeolite led to a decrease in the total condensed organic hydrocarbon phase during beech
223 pyrolysis vapours, and increased the yields of aromatic hydrocarbons. Also, H_2 production and
224 C2−C6 gas-phase hydrocarbons increased with nickel, with an emphasis on C4−C6 alkanes
225 [32]. In our work, the highest amounts of total volatiles of 63.7 % and 64.1% were obtained
226 with CeO_2 and Ni/TiO_2 respectively, but the amount of Ce loaded on the TiO_2 support was 3
227 times larger than that of Ni (see Section 3.2). Thereofre, Ni had the largest impact on the
228 microalgae decomposition, which could be linked to the fact that Ni was deposited on the
229 surface of the catalyst, while the Co and Ce were also deposited in the materials pores, as
230 indicated by the pores size distribution.
231 A large fraction of the starting microalgae was found in the gas product, with yield increasing
232 sharply according to temperature increase to 550ºC. This is due to the long residence time (60
233 min) and high cracking capacity of ceria. As for the bio-oil yields, ceria and nickel containing
234 catalysts were the most effective and the highest bio-oil yields were obtained in their presence
235 (Ce/TiO_2: 21.7 % and Ni/TiO_2: 22.5 %). This result is in agreement with our previous studies
236 on *Nannochloropsis*, *Tetraselmis* and *Isochrysis* catalytic pyrolysis, where Ni containing
237 catalysts resulted in the highest bio-oil yields and good deoxygenation effect [5,26]. These low
238 bio-oil yields can be linked to the relatively low content in fatty acids of the pyrolysed specimen
239 (20 wt%). Despite this, a notable fraction of the microalgae energy content was recovered in
240 the bio-oils. Ni/TiO_2 was the most effective maintaining 74.59 % (daf) of *Pavlova*'s energy in
241 the bio-oil, (55.72 % without catalyst) (Fig. 1). This indicates that deoxygenation of *Pavlova* in
242 the presence of nickel is very effective and can be attributed to the cracking activity of Ni and
243 synergic effect of Ni-Ti [32]. TiO_2 alone did not show any benefit in terms of increasing the
244 conversion of Pavlova, but as soon as Ni was added to the support, the reduction in char yield
245 and the increase in volatile species was clear. This agrees to a previous work, where Ni addition
246 to zeolite led to higher conversion of oxygenates and lower rate of deactivation [33].

The nitrogen distribution in the products of catalytic and non-catalytic pyrolysis of *Pavlova* at 500 °C is given in Fig 2. Bio-oil obtained without catalyst contained about 34.27 wt% of the nitrogen, while 31.21 wt% remained in the solid bio-char and 34.52 wt% went into the gas products. The use of titania based catalysts lowered the nitrogen content in the bio-oils to about 26% (from 34%). N removal was comparable with that obtained by staged hydrothermal liquefaction (1^{st} stage: 225°C, 15 min; 2^{nd} stage: 350°C, 60 min) [34]. In a previous work, the hydrodenitrogenation performance of a TiO_2-promoted Ni_2P catalyst was studied. It was found out that both the denitrogenation activity and the hydrogenation activity of Ni_2P were enhanced by the addition of TiO_2 [35]. In this work, as supported by the N content of bio-chars and bio-oils (Tables 3 and 4), the N removed from the bio-oils went in the gas phase (possibly in form of NH_3) thanks to the cracking capability of the metals loaded in the TiO_2 support. Among the catalysts, Ni and CO loaded TiO_2 were the best performing ones.

The TGA curves of the coked spent titania catalysts are shown in Fig. S4, where the mass lost between 600 and 900 °C was associated to coke combustion. Ni/TiO_2 (5.0%) had the lowest amount of coke, while Co/TiO_2 (15.3%) and $CeTiO_2$ (15%) had the highest. These results are substantially consistant with the pyrolysis mass balances (Table 2), which show their catalytic activities in terms of high total volatiles. Ni/TiO_2 and Co/TiO_2 have larger surface and pore volume compared to the other materials (see Table 1). The fact that Ni was mostly loaded in the surface of the catalyst, while Co entered the support pores, can explain the higher coke reduction capacity of the Ni/TiO_2 catalyst.

3.5. EA, TGA, ^{1}H NMR and GC–MS analyses

The HHVs and elemental analyses of the bio-chars produced at 500 °C are shown in Table 3. The produced bio-chars had carbon content between 38 and 42 wt% and HHV between 5 and 7 MJ/kg. Van Krevelen diagram showing *Pavlova*, *Chlorella* and *Nannochloropsis* bio-

chars obtained at 500°C along with coal is given in Fig. 3. As seen in Table 3 and Fig. 3, *Pavlova* bio-chars had lower HHVs than *Chlorella* and *Nannochloropsis* obtained at the same temperature. This is because most of the starting microalgae energy was recovered in the bio-oils. The *Pavlova* bio-chars have high ash and nitrogen contents, which make them suitable as soil amendment rather than solid bio-fuel. The HHVs and elemental analyses of the bio-oils are given in Table 4 and the corresponding Van Krevelen diagram is shown in Fig. 4. All bio-oils had higher HHV and lower oxygen contents than raw feedstock. Nitrogen content of bio-oils was lower in presence of catalysts decreasing from 8.75 wt% without catalyst to a minimum of 6.12 wt% in presence of Co/TiO_2. Nitrogen compounds originated from chlorophyll and proteins present in raw feedstock. Altought N was reduced, its content still represents a problem for potential NOx emission during combustion. The bio-oils produced in the presence of catalyst had higher HHVs than the one without catalyst. The most effective catalysts in improving the bio-oil quality were Ce/TiO_2 and Ni/TiO_2, which increased the HHVs of bio-oils up to about 37 MJ/kg, compared to non-catalytic run (33.32 MJ/kg). As seen in the Van Krevelen diagram (Fig. 4), the *Pavlova* bio-oils had greater HHVs than Chlorella (ZSM-5) and Nannochloropsis [5]. This indicates that not only the catalyst but also the feedstock composition affects the deoxygenation during pyrolysis. The pyrolysis bio-oils from *Pavlova* were also enriched in carbon and hydrogen content in presence of the catalysts, which makes them more suitable for fuel use compared to lignocellulose-derived bio-oils [36].

Most of the bio-oils were virtually ash free and composed of only volatiles. The bio-oil obtained with Ni/TiO_2 had the highest amount of low molecular weight volatiles while Co/TiO_2 contained the highest amount of ash (Bio-oils proximates are presented in Table S2).

The integration of selected regions of the proton-NMR spectra versus specific chemical shift ranges are presented in Table 5. NMRs, which give an overview of the chemical functionalities present in the bio-oils, show that titania catalysts altered the functionalities

297 distribution. The aliphatic proton region of the titania catalysts oils (0.0 to 1.5 ppm) was the
298 most abundant. Ni/TiO_2 had the highest percentage of aliphatic protons (~60% of all), while
299 the not metal loaded TiO_2 had the lowest (~50 % of all). The next integrated region from 1.5 to
300 3.0 ppm (aliphatic protons bonded to C=C double bond (aromatic or olefinic) or H two bonds
301 away from a heteroatom) did not show clear differences between bio-oils obtained without and
302 with catalyst. The region of the spectra (3.0-4.4 ppm) that characterises the aliphatic
303 alcohol/ether protons, or methylene groups joining two aromatic rings were less in presence of
304 Ni/TiO_2 and Co/TiO_2 (~3 %). This sharp decrease in alcohols is mainly ascribable to the
305 cracking of phytol, with Ni/TiO_2 being the most effective catalyst. The protons in the
306 carbohydrates/aromatic ether (4.4-6.0 ppm) region were found to be in small amounts (~0.5-
307 1.5 %) in all bio-oils, with lower level in presence of titania based catalysts. These results are
308 in accordance with the elemental (Table 4) and GC-MS (Table 6) analyses of bio-oils, which
309 show lower oxygen contents when the catalysts were used. The aromatic region of the spectra
310 (6.0-9.5 ppm) contain ~8-12 % of the protons in the bio-oils. This region represents both
311 hydrogen atoms in benzenoid aromatic compounds and in heteroaromatics containing nitrogen
312 and oxygen such as indole (see Table 6). All catalysts, except Ni/TiO_2, increased the percentage
313 of protons slightly in this region compared to non-catalytic run. Aldehydes and carboxylic acids
314 (9.0-10.1 ppm) were not detected in the bio-oil without catalyst and detected only in very small
315 amounts in other bio-oils. This is a clear difference with lignocellulosic bio-oils that are
316 particularly rich in oxygenated compounds. According to the proton NMR analyses, the bio-
317 oils obtained from pyrolysis of *Pavlova* contain greater percentages of the aliphatic protons.

318 GC-MS analysis of the *Pavlova* bio-oils produced at 500ºC was carried out in order to
319 determine the main products and to compare the effects of different catalysts. The list of the
320 identified compounds with main functionalities identified by GC-MS from pyrolysis of *Pavlova*
321 is given in Table 6. Bio-oils from *Pavlova* were composed of a mixture of different

functionalities such as aliphatics, monoaromatics, oxygenates, nitrogenates and polycyclic compounds. Aliphatics (alkanes and alkenes) were mainly generated during the depolymerisation of algal saturated and unsaturated fatty acids. Among the aliphatics, tridecane, tetradecane, pentadecane, neophytadiene, pentadecene, tetradecene were identified. Aliphatics are considered as valuable compounds due to their contribution to high heating value products. Represented chemical functionalities are not quite consistent with those detected by ^{1}H NMR. This can be ascribed to the different classification used for the two techniques, where tetradecanenitrile, dodecanenitrile and hexadecanenitrile, which have long-chain aliphatic parts, were not considered aliphatics in GC-MS. The main monoaromatics were phenol, phenol substitutes and benzenes, which were produced from algal components thermal cracking, metal promoted cracking, dehydration, decarbonylation and decarboxylation reactions.

Oxygenated compounds (e.g. alcohols, ethers) were not abundant in the bio-oils, while the bio-oils were rich in nitrogen containing compounds (e.g nitriles, amines and indole).

The presence of the titania catalysts affected the distribution and number of the identified chemicals. When we consider the catalysts effect, we see that TiO_2 and Ni/TiO_2 have increased the fractions of monoaromatics considerably than other catalysts. There was a clear increase in aliphatics and decrease in oxygenated compounds in the presence of all titania catalysts, which shows their good cracking properties. Among them, Ni/TiO_2 was found to be the most effective in terms of deoxygenation and denitrogenation of Pavlova bio-oils. Nitrogen compounds were also decreased (except Ce/TiO_2) in the presence of titania catalysts, indicating that TiO_2 has an active role on the O and N elimination capacity. All titania catalysts favoured the formation of polycyclic compounds in varying amounts (Table 6). This can be related to the presence of large mesopores (30-58 Å), which allow large molecules to be adsorbed and re-arranged in polyaromatic structures. The selectivity on mono-aromatics transformation in polyaromatics such as naphthalenes was linked to longer reaction times indicating that first the

depolymerised molecules form mono-aromatics and the latter form polycyclic-aromatics by secondary reactions [37].

The better activity of Ni/TiO_2 can be partially explained in terms of higher availability of Ni in surface (Co/TiO_2 has higher surface but Co is mostly loaded into the TiO_2 pores) and also can be linked to strong interaction between Ni and TiO_2 support, which lead to superior cracking capacity [38]. This is supported by the increaeed cracking of long chain alcohols such as phytol ($C_{20}H_{40}O$) and reduced presence of PAH as reported in Table 6.

4. Conclusion

The effects TiO_2 and Ni, Ce, Co loaded TiO_2 and CeO_2 catalysts on the catalytic pyrolysis of *Pavlova* microalgae was studied. The presence of Ni, Ce and CO metals supported on TiO_2 affected the product yields distribution and their quality. Presence of Ni/TiO_2 resulted in the highest bio-oil yield (22.55 wt.%) at 500 °C. In addition, the bio-oils obtained in presence of the titania catalysts had high HHV (~35-37 MJ/kg) and were effectively deoxygenated (~9-12 wt.%). Deoxygenation power decreased in this order: $Ni/TiO_2 > Ce/TiO_2 > Co/TiO_2$. Ni/TiO_2 was the catalyst that greatly affected the composition of the bio-oil, which resulted enriched in aliphatics and aromatics and depleted in O and N -compounds. The better activity of Ni/TiO_2 was related to higher availability of Ni on the catalyst surface, which also led to low coke formation and to strong interaction between Ni and TiO_2 support, which results in enhanced cracking activity.

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Figures Captions

Figure 1. Energy (daf) distribution in the pyrolysis products.

Figure 2. Nitrogen (N) distribution in the pyrolysis products.

Figure 3. Van Krevelen diagram of bio-chars.

Figure 4. Van Krevelen diagram of bio-oils.

Table 1 The physical properties of the synthesized titania supported catalysts.

Catalyst	Surface area (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)
CeO_2	18.69	71.04	0.038
TiO_2	9.48	59.06	0.015
Ce/TiO_2	126.80	29.68	0.026
Co/TiO_2	278.50	31.32	0.410
Ni/TiO_2	229.60	58.06	0.368

Table 2 The total volatiles[a] and distribution of products obtained by pyrolysis of Pavlova with (1:1 ratio) and without catalyst (Heating rate: 100 °C/min, N_2 flow rate: 545 ml/min)

Temperature (°C)	Total volatiles (%)	Solid (%)	SD	Liquid (%)	SD
	450 °C				
No catalyst	51.04	48.96	0.08	14.11	0.30
CeO_2	52.04	47.96		15.10	
TiO_2	51.82	48.18		14.44	
Ce/TiO_2	52.56	47.44	0.64	15.46	1.07
Ni/TiO_2	52.34	47.66	1.16	15.30	0.46
Co/TiO_2	51.72	48.28		15.24	
	500 °C				
No catalyst	59.10	40.90	0.14	18.68	0.25
CeO_2	62.14	37.86		21.07	
TiO_2	60.51	39.49		20.04	
Ce/TiO_2	62.54	37.46	0.91	21.67	0.05
Ni/TiO_2	62.84	37.16	0.93	22.55	0.57
Co/TiO_2	61.15	38.85		20.41	
	550 °C				
No catalyst	61.03	38.97		16.57	
CeO_2	63.74	36.26		17.82	
TiO_2	62.24	37.76	0.76	17.14	0.18
Ce/TiO_2	63.64	36.36		17.38	
Ni/TiO_2	64.10	35.90	1.99	18.71	0.25
Co/TiO_2	62.02	37.98		17.41	

[a]Mass fraction percentage of the dry and ash free feedstock.

495

496 **Table 3** The results of elemental analysis of Pavlova bio-chars obtained with titania based
497 catalysts at 500 °C.

Elemental analysis [a]	No catalyst	CeO_2	TiO_2	Ce/TiO_2	Ni/TiO_2	Co/TiO_2
Carbon	40.74	40.41	42.10	41.72	38.42	40.03
Hydrogen	1.50	1.46	1.54	1.56	1.47	1.51
Nitrogen	3.64	3.57	3.61	3.37	3.14	3.45
Oxygen[b]	54.12	54.56	52.75	53.35	56.97	55.01
H/C molar ratio	0.44	0.43	0.44	0.45	0.46	0.45
O/C molar ratio	0.99	1.01	0.94	0.96	1.11	1.03
HHV (MJ/kg)	6.18	5.93	6.94	6.74	4.84	5.79

498 [a] Weight percentage on dry and ash free basis. [b]By difference

499

500 **Table 4** The results of elemental analysis of Pavlova bio-oils obtained with titania based
501 catalysts at 500 °C.

Elemental analysis [a]	No catalyst	CeO_2	TiO_2	Ce/TiO_2	Ni/TiO_2	Co/TiO_2
Carbon	68.31	72.63	72.27	74.32	75.20	73.41
Hydrogen	8.84	9.10	9.02	9.47	9.16	9.36
Nitrogen	8.75	6.43	6.23	6.58	6.17	6.12
Oxygen[b]	14.10	11.84	12.48	9.63	9.47	11.11
H/C molar ratio	1.55	1.50	1.49	1.53	1.46	1.53
O/C molar ratio	0.15	0.12	0.13	0.10	0.09	0.11

HHV (MJ/kg)	33.32	35.56	35.21	37.07	36.95	36.33

[a] Weight percentage on dry and ash free basis. [b]By difference

Table 5 ^{1}H NMR Integrations of Pavlova bio-oils formed with titania based catalysts at 500 °C versus specific chemical shift ranges.

Chemical shift region	Proton assignment	Hydrogen content (% of all hydrogen)					
		No catalyst	CeO_2	TiO_2	Ce/TiO_2	Co/TiO_2	Ni/TiO_2
0.0 – 1.5	Alkanes	40.476	47.186	49.792	55.074	54.591	60.375
1.5 – 3.0	Aliphatics α-to heteroatom	33.324	33.124	32.655	28.051	30.875	27.185
3.0 – 4.4	Alcohols, methylene-dibenzene	11.672	7.480	4.856	4.329	3.085	3.548
4.4 – 6.0	Methoxy, carbohydrates	4.990	1.631	1.212	0.587	1.574	0.662
6.0 – 9.5	(Hetero-) aromatics	9.552	10.396	11.311	11.920	9.863	8.112
9.5 – 10.1	Aldehydes	-	0.182	0.174	0.039	0.013	0.118

Table 6 The chemical compounds present in the bio-oils obtained from Pavlova pyrolysis with titania based catalysts at 500 °C.

No	**Compounds**	**Relative abundance (% area)**					
		No catalyst	CeO_2	TiO_2	Ce/TiO_2	Co/TiO_2	Ni/TiO_2
	Monoaromatics	–			–		
1	(1-Methylbuta-1,3-dienyl)benzene	–			–	4.24	
2	1-Hexyl-4-methylbenzene	–		2.26	–	–	3.81
3	1-Phenyl-1-penten-5-ol	–		2.65	–	–	
4	2-Methyl-3-(methylthio)furan	–		2.58	–	–	

5	Benzyl nitrile	–			–	2.72	1.38
6	Benzeneacetonitrile	–		2.52	–		3.71
7	Phenol	5.77	9.01	6.69	4.32	3.99	6.83
8	Maltol	2.33				–	
9	Benzene, (methoxymethyl)-	1.26				–	
10	Phenol, 2,3-dimethyl-	–		2.71	2.90	–	4.08
11	Phenol, 2,4-dimethyl-	–	3.00		–	–	3.01
12	Phenol, 2-ethyl-	–		5.04	–		
13	1-Ethyl-1-phenylhydrazine	–		3.52	–	2.41	3.17
14	p-Cresol	5.69	7.90	5.05	4.73	4.43	5.52
15	Phenol, 2-ethyl-5-methyl-		7.30				
16	Phenol, 2-(1-methylethyl)-		3.61				
17	Phenol, 2,3,5-trimethyl-	–		–		–	5.74
18	Phenol, 2,3,6-trimethyl-	–		–	5.23	–	
19	Phenol, 2-ethyl-4-methyl-	–		–	–	–	3.22
20	2-Ethyl-6-methylphenol	2.94		–	–	–	–
21	Phenol, 3-ethyl-	5.47	3.86	4.46	–	2.22	–
22	3-Methyl-4-ethylphenol			–	–	4.45	–
23	2,4-Diethylphenol			–	–	–	2.15
24	2,5-Diethylphenol	1.56		–	–	–	
25	Phenol, 3-amino-	2.05		–	–	–	
26	N-(1-methyl-2-propynyl)aniline			2.58	3.20	–	2.80
27	Furoxan, 4-nitro-3-phenyl-, 2-oxide				5.42	3.61	2.41
		27.07	**34.68**	**40.06**	**25.80**	**28.07**	**47.83**
	Aliphatics						
28	Tridecane	–		1.69	–	1.75	2.71
29	Tetradecane	–		2.55	–	1.77	2.33
30	2-Tetradecene, (E)-	–			–	1.35	
31	Pentadecane	1.98		2.39	1.88	2.32	5.14
32	2-Methyl-Z-4-tetradecene	–		–	–	0.82	
33	1-Pentadecene	–		–	–	3.21	
34	2-Pentadecene	–		–	–		4.02
35	2,6,10-Trimethyl,14-ethylene-14-pentadecane	–			8.23	6.33	–
36	5-t-Butyl-cycloheptene			6.78			–

37	4-Chloro-2-(chloromethyl)-1-butene			1.16			–
38	Neophytadiene		7.90				
		1.98	**7.90**	**14.57**	**10.11**	**17.55**	**14.20**
	Oxygenated compounds						
39	Decyl acetate	–		–	–	1.58	
40	Pentanoic acid	–		–	–		0.81
41	Octanoic acid	–		–	–	1.92	
42	1-Cyclohexyl-2-methyl-prop-2-	–			–	3.19	
43	1-Tetradecanol	–		2.65	–	–	1.36
44	Butanoic acid	–		1.29	–	–	1.07
45	Pentane, 2-methoxy-	–	0.77		–	–	1.33
46	3-Acetoxy-5-(acetoxymethyl)cyclohexene	–		3.42	–	–	
47	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	–		–	–	–	5.19
48	Dimethyl Sulfoxide	2.45		–	–	–	–
49	Dodecanoic acid, 4-methyl-, methyl ester	1.06		–	–	–	–
50	dl-Erythro-O-methylthreonine	1.26		–	–	–	–
51	(-)-(3S,4R,5R)-3-Azido-4-hydroxy-5-methyldihydro-2-(3h)-furanone	1.39		–	–	–	–
52	2-Butenoic acid, 3-ethoxy-, ethyl ester	0.57		–	–	–	–
53	6-Isopropyl-3-methyl-2-cyclohexen-1-ol			3.36	–	–	–
54	Cis-chrysanthenol			–	4.07	–	–
55	Methyl phenyl(2-piperidinyl) acetate	2.45		–	–		–
56	4-Heptenoic acid, 3,3-dimethyl-6-oxo-, methyl ester			–	–	2.93	–
	2-Cyclopenten-1-one, 3-(1-methylethyl)-	2.23		–	–	–	–
57	(+)-(1S,6R)-6-Phenyl-2-cyclohexene-1-carboxylic acid	0.82		–	–	–	–
58	S-Butyl ester of .alpha.-phenylbenzeneethanethioic acid	2.72		–	–	–	–
59	Isobutyric acid, tetradecyl ester		10.8				
60	Phytol	20.93	10.8	6.32	5.19	5.93	4.47

		35.88	**22.4**	**17.04**	**9.26**	**15.55**	**14.23**
	Nitrogen compounds						
61	Benzenepentanamide			–	5.23	–	
62	5-Hepten-2-amine, N,6-dimethyl-		1.28				
63	Propanamide	1.39	0.94	–	–	–	
64	Pyridine, 3-phenyl-			–	–	–	1.72
65	Pyrrolidine, 1-acetyl-	0.57		–	–	–	–
66	Hexahydro-2(1H)-azocinone	1.11		–	–	–	–
67	Butanamide, 3-methyl-	2.03		–	–	–	–
68	N-(1-Methylethylidene)-2-propanamine	0.99		–	–	–	–
69	Butanamide, 3-methyl-	2.08		–	–	–	–
70	Benzenepropanenitrile	7.37	5.67	5.30	3.35	3.61	3.16
71	2-Piperidinone	1,16					
72	Cyclohexanamine, N-cyclopentylidene-					3.48	
73	Tetradecanenitrile	4.31		1.53	13.67	6.90	1.78
74	Pyridine, 4-phenyl-				1.63		
75	1-Buta-1,3-dienyl-pyrrolidine	5.44					
76	N-Ethyl-hexahydro-1H-azepine		2.92				
77	Octanamide		2.06				
78	Hexadecanenitrile	1.66	8.62	2.61	4.88	2.76	2.24
79	Dodecanenitrile		6,1				
80	Indole	4.95	6.25	5.23	7.01	4.68	3.57
81	1H-Indole, 2-methyl-	–	1.04	–	1.58		
82	1H-Indole, 5-methyl-	–		–			0.77
83	1H-Indole, 4-methyl-	–		–		0.80	
84	1H-Indole, 1-ethyl-	–				1.03	–
85	Benzonitrile, 2,4,6-trimethyl-	–			0.66	–	–
86	7-Methyl-1H-indole	–		1.42	–	–	–
87	1H-Indole, 3-methyl-	1.04			–	–	1.03
88	5-(1H-Indol-3-ylmethyl)-2-thioxo-4-imidazolidinone	0.97			–		
		35.07	**34.9**	**16.09**	**38.01**	**23.26**	**14.27**
	Polycyclic compounds						

89	1H-Indene, 1-methylene-	–				1.14	2.63
90	Naphthalene, 2-methyl-	–		7.46	1.68	3.71	
91	Naphthalene, 1-methyl-	–		–	3.76	4.71	2.63
92	Naphthalene, 1,3-dimethyl-	–		–		6.01	
93	Naphthalene, 1,5-dimethyl-	–		–		–	4.21
94	Naphthalene, 2,7-dimethyl-	–		–	7.42	–	–
95	Naphthalene, 2,6-dimethyl-	–		4.78		–	–
96	Naphthalene, 3-(1-methoxyethyl)-1- methyl-	–			3.96		–
		0	**0**	**12.24**	**16.82**	**15.57**	**9.47**
	Total	**100**	**100**	**100**	**100**	**100**	**100**

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